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First-principles studies of the electronic structure of cyclopentene on Si(001): density functional theory and GW calculations

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The electronic structure and ground-state geometry of cyclopentene monolayers on Si(001) are studied using ab initio pseudopotential density-functional theory (DFT). Quasiparticle excitation spectra are calculated within the GW approximation. Both *cis* and *trans* cyclopentene monolayers are considered. In both geometries, a strong electronic coupling between the monolayer and Si substrate is found; substantial inter-molecular interactions are present, as indicated by broadening in molecular levels that are decoupled from the substrate. It is argued that the *cis* structure is kinetically favored, and we evaluate self-energy corrections to the eigenstates of this configuration near the band edges within the GW approximation. The calculated self-energy corrections are large, exceeding those of bulk Si, and increase the energy gap between occupied and unoccupied frontier adsorbate states by 1.3 eV.

1 Introduction

Hybrid organic/silicon devices have attracted considerable attention of late because of their potential use in a variety of electronic applications [1–4]. Several recent experimental studies have reported the fabrication and characterization of ordered, self-assembled monolayers of organics on Si(001) [5–7]. The homogeneous structure of these monolayer-thin organic films, as well as their ability to form strong covalent bonds with the underlying Si substrate, make them extremely promising for integration with silicon microelectronics technology. Central to the ultimate realization of organic/silicon devices, of course, is the ability to understand and control the nature of electronic coupling between the organic layer and silicon substrate. Of particular importance is the impact of the substrate on electronic states in the organic layer, as governed, for example, by the local surface chemistry associated with the system. In this work, we perform first-principles calculations to explore the atomic and electronic structure of cyclopentene monolayers on Si(001), prototypical ordered organic/silicon systems.

The clean Si(001) surface is characterized by ordered rows of Si dimers, which provide an ideal template for the growth of ordered molecular layers. Scanning tunneling microscopy and infrared vibrational spectroscopy have shown that cyclopentene (C_5H_8) can form monolayers on Si(001), with each molecule

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oriented along a single Si dimer [7]. This orientation is consistent with a cycloaddition mechanism for alkenes on Si(001), where the alkene π bond breaks to form two new σ C−Si bonds with the Si dimer atoms. The atomic structure of an ordered cyclopentene monolayer (ML) on Si(001) has also been thoroughly examined with density functional theory (DFT) [8−10]. The structural geometries reported in these previous DFT studies are consistent with experimental observations [7]. The so-called *cis* structure, with H atoms closest to Si residing on the same side of C_5H_8, is most commonly studied [7−10], although an alternative *trans* structure (H atoms on opposite sides of C_5H_8) has also been proposed theoretically [10]. In the following, we shall discuss the atomic and electronic structure of these two geometries, with specific focus on the local surface electronic structure in a range of energies near the Si band edges.

2 Methods

To examine the geometry and electronic structure of cyclopentene monolayers on Si(001), we perform calculations within two levels of theory. First, DFT calculations are used to optimize the geometry and provide some qualitative insight into the surface electronic structure. Next, we compute quasiparticle excitation energies, using the DFT Kohn−Sham eigenstates to construct the self-energy operator within the GW approximation [11, 12]. Here G is the electron Green's function and W is the dynamically screened Coulomb interaction. This many-body approach allows treatment of the molecule and substrate at the same level of theory. Previous work involving an ethylene monolayer on Si(001) obtained an electronic spectrum within the GW approximation in quantitative agreement with photoemission experiments [13].

The ground-state DFT calculations are performed using two different plane-wave pseudopotential implementations, the VASP [14] and PARATEC [15, 16] codes; excellent agreement is obtained between the two codes. In VASP, we use the projected augmented wave method [17] with an energy cutoff of 29 Ry. Norm-conserving Troullier−Martins pseudopotentials [18] are employed in PARATEC, with an energy cutoff of 50 Ry. Reciprocal space is sampled with a Monkhorst-Pack *k*-point mesh of $2 \times 4 \times 1$ per unit supercell. The local density approximation (LDA) for the exchange-correlation functional is employed. We find that LDA gave comparable results with the generalized gradient approximation (GGA), as parametrized by Perdew−Burke−Ernzerhof, for atomic structures and relative energetics between the *cis* and *trans* structures (Table 1). We simulate the Si(001) surface using a slab of 6 Si layers terminated by H atoms on the bottom side, and Si surface dimers on the top. Doubling the slab thickness to 12 Si layers does not change the atomic structure or binding energies significantly (Table 1). In each case, the theoretical lattice constant for Si (VASP LDA: 5.40 Å, PARATEC LDA: 5.39 Å) is used, and the bottom 2 Si layers are fixed to their bulk positions. All other atoms are allowed to relax until their forces are <0.01 eV/Å. At least 13 Å of vacuum is used between Si slabs.

The details of our GW calculations are described elsewhere [11, 12]. An energy cutoff of 50 Ry and a *k*-point mesh of $2 \times 4 \times 1$ are used to obtain the DFT-LDA wavefunctions and energies. A vacuum re-

Table 1 Binding energy (eV/molecule) of 1 ML C_5H_8 on Si(001). Our results, in bold, are obtained using Si slabs with 6 Si layers, except for values in brackets which use 12 Si layers.

		cis	*trans*
PARATEC	**LDA**	**2.07**	**–**
VASP	**LDA**	**2.14 (2.11)**	**2.13 (2.10)**
Ref. [10]	LDA	1.4	1.6
VASP	**GGA**	**1.22 (1.19)**	**1.22 (1.20)**
Ref. [8]	GGA	1.17	–
Ref. [9]	GGA	1.05	0.94
Ref. [10]	GGA	0.6	0.8

gion of 19.4 Å is kept between Si slabs, corresponding to a closest distance of 13.4 Å between the H atoms terminating the bottom of the Si slabs and molecular atoms on adjacent slabs. A total of 770 conduction bands (with energies of up to ~51 eV above the Si valence band maximum) are included in the evaluation of the self-energy. The dielectric matrices are expanded in reciprocal space up to an energy cutoff of 9 Ry. Increasing the energy cutoffs or number of conduction bands does not change the quasiparticle energies by more than 0.1 eV. The GW parameters for bulk Si are converged to a level of accuracy consistent with the slab calculations.

3 Results and discussion

As shown in Table 1, the binding energies we obtain compare well with those from other plane-wave calculations [8, 9], although they differ from [10], possibly due to a difference in basis set. The LDA binding energies are significantly larger than the GGA values (in agreement with Ref. [10]), due to the tendency of the LDA to overbind.

In Fig. 1, we show views of relaxed geometries for full (1 ML) coverage with C_5H_8 in (a) *cis* and (b) *trans* configurations. These structures have very similar total energies (Table 1). Figure 2 shows a comparison of the partial densities of states (DOS) of the two structures, computed from LDA Kohn–Sham eigenvalues and projected onto spherical harmonics in spheres centered on C (radii 0.86 Å) and H (radii 0.37 Å). The partial DOS plots are obtained using the tetrahedron method with Blochl corrections [19], with a Brillouin Zone *k*-point sampling of 4 × 8 × 1 (16 irreducible *k*-points). Energies are referenced relative to the bulk Si valence band maximum (VBM), obtained by aligning the average local potential in the middle of the Si slabs with that of bulk Si. The partial DOS indicate that the electronic spectra of the molecular layers in both structures are far from discrete, with significant dispersion for energies above –12 eV. This is consistent with a strong electronic coupling of the molecule to the substrate, which we expect from the covalent C–Si bonds and strained interface geometry. (The angle between bonds, C_{bot}–Si_{top} and Si_{top}–Si_{top}, is 78°, in contrast to bond angles of ~109° in unstrained tetrahedral sp^3 coordination for the Si atom.) The Si valence bandwidth is 12 eV, suggesting that the molecular states with energies above –12 eV are resonant with the propagating states in the Si substrate. Examination of the surface projected band structure confirms this picture, indicating very few gaps and strong electronic coupling to the substrate for most states. However, the relatively sharp peaks in the DOS at –13.6 and –16.9 eV are molecular states essentially decoupled from Si; the dispersion of 0.4–0.6 eV observed for these states is owing to significant intermolecular interactions within the monolayer. Although the DOS for these decoupled molecular states are similar for both *cis* and *trans* structures, detailed differences are visible between both geometries above –12 eV, indicating that the electronic structure closer to the VBM is more sensitive to the details of atomic structure.

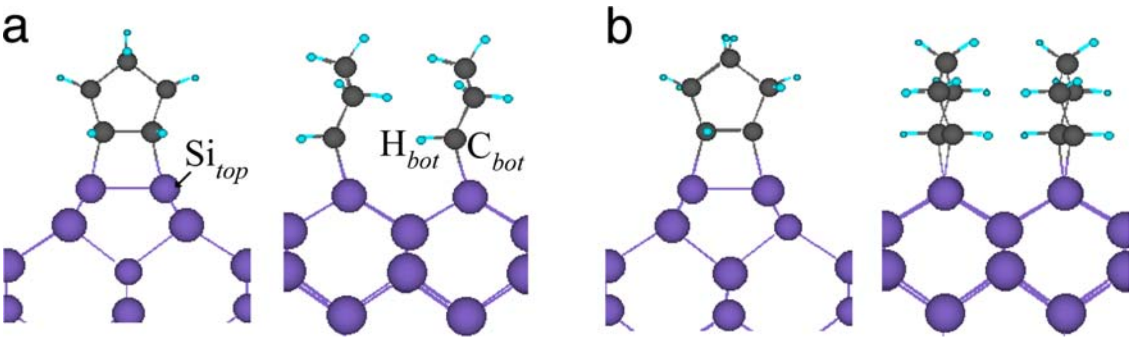

Fig. 1 (online colour at: www.pss-b.com) Atomic structure of 1ML C_5H_8 on Si(001) in (a) *cis* and (b) *trans* configurations. The left and right panels provide two different views, down and perpendicular to the Si(001) dimer rows respectively. In each case, only four Si layers are shown.

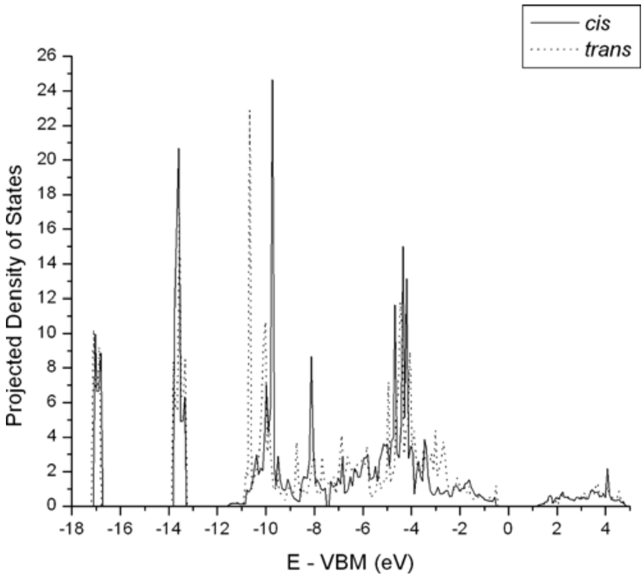

Fig. 2 LDA DOS projected onto spherical harmonics in spheres centered on C (radii 0.86 Å) and H (radii 0.37 Å) in the molecule, summed over s, p and d.

Although the *cis* and *trans* structures have similar total energies, the *cis* configuration is kinetically favored because of the symmetry of the frontier orbitals and the ring shape of the molecule [9]. Furthermore, the *cis* arrangement is computed to be about 0.4 eV more stable than *trans* at 0.5 ML coverage. This suggests that a 1 ML *trans* structure can form only if *cis* transforms to *trans* with increasing coverage, a process that involves breaking of C–Si bonds and thus is likely to be kinetically hindered. For these reasons, we shall focus the remainder of our discussion on the *cis* structure. In particular, we shall examine results of quasiparticle calculations within the GW approximation for this geometry. We focus on states with energies within 3 eV of the VBM, as states outside this energy window are less important for transport and optical spectroscopic properties. Unlike the DFT Kohn–Sham eigenvalues, our calculated quasiparticle energies take electron correlation into account directly through the self-energy operator and provide quantitative spectral information within this energy window.

Figure 3 shows the molecular weights of eigenstates near the band edges, as a function of their LDA Kohn–Sham energies and GW quasiparticle energies, for two high symmetry points in the Brillouin Zone, Γ and K. The LDA energies are referenced relative to the LDA value of the Si VBM, and the GW energies relative to the GW values of the Si VBM. The molecular weight is defined here as the integral of the square of the wavefunction over a spatial region containing the molecular layer; unity weight indicates the wavefunction is completely localized within the chosen region. The spatial region considered here is parallel to the Si surface plane, and extends from 1 Å above the molecule down to a height midway between the plane of C_{bot}'s and Si_{top}'s (following the nomenclature defined in Fig. 1). Importantly, the molecular weights in Fig. 3 are all <0.5; in contrast, molecular weights of >0.9 were computed for some eigenstates that lie outside this energy window. This reflects the fact that the states within this energy window ([–3, 3] eV relative to the Si VBM) extend into the bulk and are not well localized on the molecular layer; their small molecular weights are associated with the C_{bot}–Si_{top} bonds, and in some cases with C_{bot}–H_{bot} as well. We shall refer to these states as frontier adsorbate states.

The energy levels of the adsorbate states relative to the Si band edges are experimentally relevant quantities, since the Fermi level of degenerately-doped Si can be aligned with either the VBM or CBM depending on whether the dopants are p- or n-type, respectively. Our calculations show that, in contrast to the clean (2 × 1)-reconstructed Si(001) surface [20], the 1 ML C_5H_8/Si(001) system has no surface or

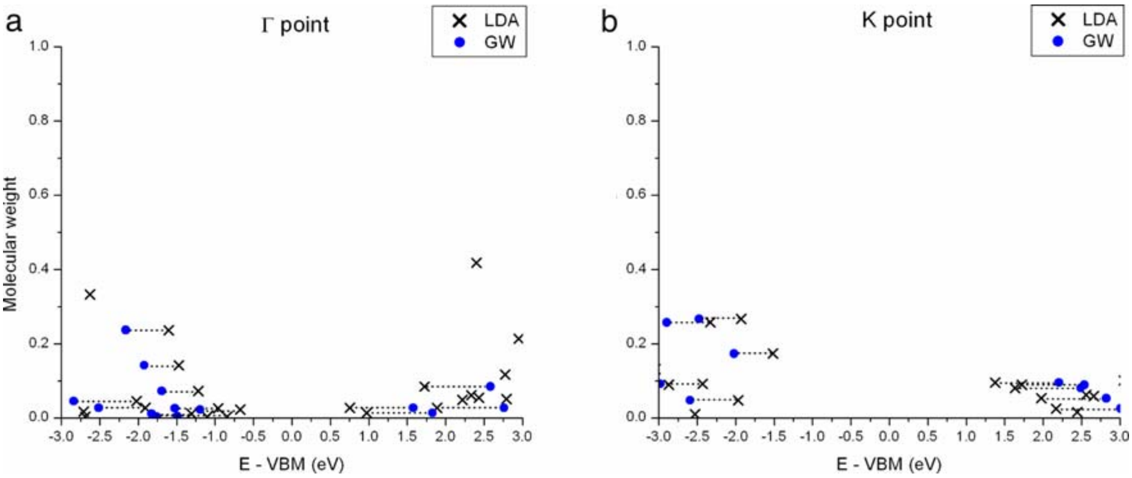

Fig. 3 (online colour at: www.pss-b.com) Calculated molecular weights of eigenstates as a function of LDA and GW energy levels, at high symmetry points (a) Γ and (b) K in the Brillouin Zone. The zero of energy, 'VBM', corresponds to the LDA value of the Si VBM for the LDA plots, and the GW value for the GW plots. As a guide, dotted lines are used to join GW (dots) and LDA (crosses) data-points that correspond to the same eigenstates.

adsorbate states in the band gap of bulk Si. This is consistent with the saturation of dangling bonds associated with the bare Si(001) surface dimers, resulting from cyclopentene adsorption.

The self-energy corrections we compute near the band edges are significant. The occupied adsorbate states are shifted –0.5 to –0.6 eV away from the Si VBM (accounting for the self-energy correction for VBM in bulk Si, as in Fig. 3). Similarly, unoccupied adsorbate states are shifted +0.8 to +0.9 eV further above the Si VBM. The self-energy correction in 1 ML C_5H_8/Si(001) thus increases the energy gap between the occupied and unoccupied frontier adsorbate states substantially, by about 1.3 eV. These corrections we compute here are larger than those calculated for the surface dimer states on clean (2 × 1)-reconstructed Si(001), which were reported to be between –0.10 eV to +0.15 eV for the occupied dimer state, and between +0.35 eV to +0.50 eV for the unoccupied dimer state [20]. We also obtain energy shifts relative to the Si CBM, which requires computation of the self-energy correction for the Si CBM as well. We find that corrections to the Si VBM and CBM cause the fundamental gap of bulk Si to increase by 0.7 eV, from its LDA value of 0.5 eV to 1.2 eV, the latter being in excellent agreement with experiment [12]. As a result, the frontier unoccupied adsorbate states are shifted by +0.1 to +0.2 eV away from the Si CBM.

Because of the strong electronic coupling between the molecular monolayer and Si substrate, it is difficult to associate specific energies with the frontier adsorbate states. For simplicity, we define the highest-occupied frontier adsorbate state as the highest-occupied state with a molecular weight of more than 0.2 (first peak below the Si VBM in Fig. 3). This has a quasiparticle energy of –2.2 eV at the Γ point (Fig. 3(a)) and –2.5 eV at the K point (Fig. 3(b)) (relative to the Si VBM). Although there are no evident peaks above the CBM for the quasiparticle states in Fig. 3, we find that those unoccupied states with molecular weights of ~0.1 are partially localized on $H_{bot}–C_{bot}–Si_{top}$. The lowest-unoccupied state of this nature has a quasiparticle energy that is 1.4 eV above the CBM at the Γ point, and 1.0 eV above the CBM at the K point.

4 Conclusion

In conclusion, we have studied the atomic and electronic structure of ordered monolayers of cyclopentene on Si(001). Our results show that the cyclopentene monolayers exhibit strong electronic coupling to the Si substrate, and the projected densities of states close to the Si VBM are sensitive to the details of atomic structure. We argue that cyclopentene binds to Si dimers in a *cis* configuration. We have further analyzed the electronic structure of the *cis* structure by calculating its quasiparticle energy spectrum within the GW approximation. The resulting self-energy corrections enhance the gap between occupied and unoccupied frontier adsorbate states by about 1.3 eV. The GW calculations reported here allow a quantitative description of the energies of the frontier adsorbate states, which can be compared directly with experiments. Further details of the electronic structure of this system and of lower coverage systems will be reported elsewhere.

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